PTO 04-2181

Japanese Patent

Document No. 2000-243392

ANODIC ACTIVE MATERIAL, METHOD FOR MANUFACTURING THE SAME, AND LITHIUM ION SECONDARY BATTERY WHICH USES THE AFOREMENTIONED ANODIC ACTIVE MATERIAL

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UNITED STATES PATENT AND TRADEMARK OFFICE

Washington, D.C. March 2004

Translated by: Schreiber Translations, Inc.

Country	:	Japan
Document No.	:	2000-243392
Document Type	:	Kokai
Language	:	Japanese
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Applicant	:	Mitsubishi Electric Corp.
IPC	:	H 01 M 4/58 C 01 G 49/00 51/00 53/00 H 01 M 4/02 10/40
Application Date	:	February 16, 1999
Publication Date	:	September 8, 2000
Foreign Language Title	:	Seikyoku Katsu Busshitsu Oyobi Sono Seizo Hoho Narabini Joki Seikyoku Katsu Busshitsu o Mochiita Richiumu Ion Niji Denchi
English Title	:	ANODIC ACTIVE MATERIAL, METHOD FOR MANUFACTURING THE SAME, AND LITHIUM ION SECONDARY BATTERY WHICH USES THE AFOREMENTIONED ANODIC ACTIVE MATERIAL

(54) Title of the invention

ANODIC ACTIVE MATERIAL, METHOD FOR MANUFACTURING THE SAME, AND LITHIUM ION SECONDARY BATTERY WHICH USED THE AFOREMENTIONED ANODIC ACTIVE MATERIAL

A lithium ion secondary battery which uses the aforementioned anodic active material

(57) Summary

Objective: Ferrite can be effectively utilized, and a lithium ion secondary battery endowed with favorable performances can be inexpensively manufactured by using it.

Solution mechanism: A solution into which a composite oxide (ferrite) which includes, a main component, a composition represented by the following general formula: AFe_2O_4 (in the formula, A signifies Mn, Fe, Zn, Co, Ni, or Cr) has been solubilized is prepared, whereas a solution is obtained by mixing said solution with an inorganic salt which includes a lithium ion, an inorganic salt which includes a Co, Ni, Mn, or Fe (transition metal element) ion, and a complexifying agent which forms a complex of lithium and the aforementioned transition metal in such a way that the ratio of lithium ions and ions of the aforementioned transition metal elements will be 1 : x ($0.5 \leq x \leq 1.0$), whereas a precursor is obtained by removing the solvent of

[1] Numbers in the margin indicate pagination in the foreign text.

said solution by means of spray dry, whereas the obtained precursor is thermally treated.

Patent Claims /2

Claim 1

A method for manufacturing an anodic active material inclusive of a process whereby a solution into which a composite oxide that includes, as a main component, a composition represented by the following general formula: AFe_2O_4 (in the formula, A signifies Mn, Fe, Zn, Co, Ni, or Cr) has been solubilized and another solution wherein an inorganic salt that includes a lithium ion, an inorganic salt that includes at least one type of first metal element ion(s) selected from among Co, Ni, Mn, and Fe, and a complexifying agent that forms a complex of lithium and the aforementioned first metal element(s) are mixed with one another in such a way that the ratio of lithium ions and ions of the aforementioned first metal element(s) will be 1 : x ($0.5 \leq x \leq 1.0$) are obtained, a process whereby a precursor is obtained by removing the solvent(s) of the aforementioned solutions by means of a spray dry, and a process whereby the aforementioned precursor is thermally treated.

Claim 2

A method for manufacturing an anodic active material specified in Claim 1 characterized by the fact that the inorganic salt which includes a lithium ion is lithium nitrate, lithium

sulfate, lithium chloride, lithium fluoride, lithium acetate, or lithium hydroxide.

Claim 3

A method for manufacturing an anodic active material specified in Claim 1 or 2 characterized by the fact that the inorganic salt which includes the first metal element ion(s) is a nitrate, sulfate, chloride, acetate, fluoride, or hydroxide.

Claim 4

A method for manufacturing an anodic active material specified in any one of Claims 1 through 3 characterized by the fact that the complexifying agent is oxalic acid, tartaric acid, citric acid, succinic acid, malonic acid, or maleic acid.

Claim 5

An anodic active material which is obtained by the manufacturing method specified in any one of Claims 1 through 4 and which includes a main component represented by the following general formula: LiM_xO_2 (in the formula, M is Co, Ni, Mn, or Fe, whereas $0.5 \leq x \leq 1.0$).

Claim 6

An anodic active material which is obtained by the manufacturing method specified in any one of Claims 1 through 4 by using a composite oxide which includes $CoFe_2O_4$ and $NiFe_2O_4$ as main components.

Claim 7

An anodic active material which is obtained by the manufacturing method specified in any one of Claims 1 through 4 by using a composite oxide which includes $MnFe_2O_4$ as a main component.

Claim 8

A lithium ion secondary battery with the following characteristics: In a lithium ion secondary battery constituted to possess an anodic active material layer, a cathodic active material layer, and a separator which retains a non-aqueous electrolyte inclusive of a lithium ion and which is configured between the aforementioned anodic and cathodic active material layers, the aforementioned anodic active material layer includes the anodic active material specified in any one of Claims 5 through 7.

Detailed explanation of the invention

[0001]

(Technical fields to which the invention belongs)

The present invention concerns an anodic active material designed to be used within a lithium ion secondary battery which includes a non-aqueous solution as an electrolyte, a method for manufacturing the same, and a lithium ion secondary battery which uses the same.

[0002]

(Prior art)

Attempts have been made in recent years to reduce the sizes of electronic appliances such as portable phones, portable terminals, etc., and batteries to be used for such appliances are required to meet higher voltage and/or higher capacitance requirements as well. It is against such a backdrop that lithium ion secondary batteries which include, as electrolytes, non-aqueous solutions with high retrievable capacitances per unit weight have come to bear great expectations, and attempts are being made to develop them in diverse fields.

[0003]

A laminar compound which enables an electrochemical intake and release of lithium is used as the anodic active material of such a lithium ion secondary battery, and active materials expressed by the following general formula: $Li_y\alpha O_2$ ($0.5 \le y \le 1.0$), namely composite oxides of lithium and transition metals expressed by $Li\alpha O_2$ and $Li\alpha_2O_4$ (wherein α is a transition metal element) such as $LiCoO_2$, $LiNiO_2$, $LiFeO_2$, $LiMn_2O_4$, etc., are being used.

[0004]

Under normal circumstances, the aforementioned composite oxide may, for example, be obtained, as U.S. Patent Nos. 4,302,518 and 4,980,080 note, by mixing a transition metal oxide or hydroxide compound (e.g., nickel oxide, cobalt oxide, manganese dioxide, etc.) with a lithium-containing compound (e.g., lithium carbonate, lithium oxide, etc.) at a certain ratio and by then

baking the obtained mixture in an air or oxygen atmosphere within a temperature range of 700 ~ 900°C for 1 to several hours.

[0005]

For purposes of upgrading the capacitance and of improving the recharge & discharge cycle performances, furthermore, Japanese Patent Application Publication Kokai No. Sho 63[1988]-299056 Gazette notes the composition of $LiNi_zCo_{1-z}O_2$, which represents a combination of the aforementioned composite oxides, whereas Japanese Patent Application Publication Kokai No. Hei 5[1993]-242891 Gazette notes an embodiment in which miniscule quantitative ratios of such elements as Al, Ti, etc. are added. Thus, extremely large numbers have been proposed as examples of elements added at miniscule quantitative ratios.

[0006]

Of these active materials, however, only $LiCoO_2$, which is relatively stable and which yields a high capacitance, is being used for practical purposes at present, and there still exists room for the improvement of the capacitance, which is far from the theoretical value.

[0007]

This active material can be obtained by mixing, based on the dry format, a lithium-containing compound (e.g., lithium carbonate, lithium oxide, lithium hydroxide, etc.) and a cobalt-containing compound (e.g., cobalt oxide, cobalt hydroxide, etc.) and by then baking the obtained mixture at a high temperature of approximately 900°C. This composite oxide can be synthesized with

relative ease, and therefore, it is often synthesized based on an ordinary dry method, but since the homogeneous mixing capacity of the dry method is limited, it becomes difficult, due to a specific gravity differential, to obtain a homogeneous mixture in a case where a lithium-containing compound with a low specific gravity is mixed with a transition metal-containing compound with a high specific gravity based on the dry method. The heterogeneity of the obtained mixed powder in turn contributes to the heterogeneity and defects of the active material crystal, and since the mobilization of the lithium ion within the laminar structure of the active material becomes hindered, the battery capacitance diminishes. The laminar structure of such a disorderly portion, furthermore, is unstable, and since the interlayer coupling force is tenuous, the laminated structure becomes destroyed as a result of the entry and/or exist of a lithium ion, which in turn contributes to the deterioration of the repetitive recharge & discharge cycle performances. As can be inferred from the foregoing discussion, the capacitances of the aforementioned composite oxides obtained by the aforementioned manufacturing methods of the prior art are still far from their theoretical equivalents, and there accordingly remains room for improvement. /3

[0008]

Attempts, furthermore, are being made, for the purpose of homogeneously mixing the respective elements that constitute an active material, to resort to a wet method wherein a salt of a

lithium-containing compound and a salt of a transition metal-containing compound are each solubilized into water and wherein the respective aqueous solutions are mixed with another in an ionic state. Such attempts may, for example, be instantiated, as Japanese Patent Application Publication Kokai No. Hei 5[1993]-325966 Gazette and Japanese Patent Application Publication Kokai No. Hei 6[1994]-44970 Gazette note, by a method wherein the respective salts of nickel and lithium are solubilized into an appropriate solvent and mutually mixed based on the so-called "wet format" and wherein the obtained mixture is baked for obtaining an active material.

[0009]

As far as these examples are concerned, an extremely homogeneous mixture can be obtained in an aqueous solution state, for the lithium and transition metal have thereby been mixed with one another in an ionic state, although it is impossible to perpetuate the homogeneous state in the course of the removal of the solvent (e.g., water, etc.), whereas, on the contrary, a locally deposited salt becomes formed together with coexisting anionic species, and since the respective components come to exist in mutually separated states, it is extremely difficult to obtain the targeted homogeneous precursor, which is problematic.

[0010]

In an attempt to solve this problem, a method wherein an appropriate precipitation agent is added for the purpose of formulating a coprecipitate salt comprised of multiple types of

ions (i.e., coprecipitation method), a method wherein a complexifying agent designed to form a composite complex together with cations existing within a solution for the purpose of obtaining a precursor (i.e., complex polymerization method), etc. are being investigated. It has come to be known that, according to such measures, both cations, namely the lithium ion and transition metal ion in this case, come to form a coprecipitate or composite complex and that, as a consequence, the homogeneity of the precursor in the ionically mixed state can be preserved. Japanese Patent Application Publication Kokai No. Hei 6[1994]-203834 Gazette, for example, notes a method wherein ethylene glycol is added to the respective acetates of lithium and a transition metal for forming and then gelling a composite alcoholate and wherein said composite product is then baked for obtaining an active material, whereas the respective Gazettes of Japanese Patent Application Publication Kokai Nos. Hei 6[1994]-163046 and Hei 7[1995]-142065 disclose a method wherein a salt of a lithium-containing compound and a salt of a transition metal-containing compound are gelled together with an aqueous citric acid solution and wherein the obtained product is baked for obtaining an active material.

[0011]

As far as the aforementioned former, namely coprecipitation, method is concerned, however, it is theoretically difficult to induce the coprecipitation of elements with vastly different chemical attributes, as in the case of the alkali metal ion and

transition metal ion, due to which separate precipitates inevitably become generated, and thus, it is difficult to achieve the objective homogeneity of the precipitate based on this method.

[0012]

The latter, namely complex polymerization, method represents a mechanism for removing a solvent from a composite complex. Complex ions may come to exist, as a result of the formation of a complex by multiple types of element ions, within a solution in a case where various complexifying agents are used, but it is not necessarily possible to perpetuate this state in the course of the removal of a solvent, as a result of which a precursor with a poor homogeneity no different from its counterpart of the dry method often becomes obtained. In the context of inducing the above-mentioned reaction of ethylene glycol and citric acid, a polycondensing reaction is induced to progress by gradually removing the solvent, but an extremely long reaction period is necessary, whereas the temporarily generated gel becomes re-solubilized by the unremoved water content and/or water content of air, and since a salt becomes formed and deposited together with coexisting anions such as acetic acid roots, nitric acid roots, etc., a compositional distortion occurs, as a result of which the precious homogeneity attained at the complex stage becomes lost. In the context of synthesizing an active material to which the pervasion of water is extremely inauspicious, as in the case of the active material targeted by the present invention, furthermore, these wet methods are inappropriate, for they entail

the possibility of the persistence of residual water at the precursor stage. All of these reactions, furthermore, are accompanied by gelation, and therefore, the obtained precursors are inevitably viscous gels with high hygroscopic tendencies and poor handling friendlinesses, due to which the handling of the gel becomes a grave problem. These methods, furthermore, require large quantities of coprecipitation agents and/or complexifying agents such as ethylene glycol, etc., and since convoluted manufacturing processes (e.g., reduced pressure drying, etc.) are involved, the yield of the precursor is low, which, too, is problematic. Although these methods may be said to be suitable for manufacturing powders used for special purposes, they cannot be said to represent a realistic method for synthesizing an active material which must meet quantitative requirements specific to battery applications.

[0013]

The spray dry method, on the other hand, is known as another powder synthesizing method. This method is often orchestrated for the purpose of granulation, although it has also been reported as a method for synthesizing an active material. As is mentioned in extant literature [*Solid State Ionics*, **44** (1990), pp. 87 ~ 97], for example, an embodiment in which a slurry is prepared by mixing an aqueous LiOH solution and an $Ni(OH)_2$ powder, in which a precursor wherein the surface of the $Ni(OH)_2$ powder is coated with LiOH is prepared by spray drying the obtained slurry, and in which an active material is obtained by baking said precursor is

proposed as a method for synthesizing $LiNiO_2$, whereas Japanese Patent Application Publication Kokai No. Hei 2[1990]-9722 Gazette discloses, as a method for manufacturing a manganese oxide powder, an embodiment in which the respective aqueous solutions of a manganese-containing compound and a lithium-containing compound are sprayed by using an ultrasonic humidifier and wherein an active material is obtained by baking the obtained product. These methods, however, are being used for coating particle surfaces or for removing solvents and are not active material synthesis methods which favor mass production. The precursor obtained from an aqueous solution of the raw ingredient components alone, furthermore, is extremely hygroscopic, and therefore, its handling is problematic.

[0014]

In other words, from the standpoint of obtaining a high-performance active material, it is extremely important to orchestrate the wet method, which is advantageous over the dry method in terms of homogeneity, and to optimize the solution composition and solvent removal method for enabling the procurement of a precursor which inherits the homogeneous mixing state of the active material composition in a solution state. It is in this context that a method for obtaining an active material which inherits the homogeneity of the ionic state based on the spray dry format (World Patent Gazette WO98/29915) was orchestrated, as a result of which it was discovered that the aforementioned manufacturing method characterized by the use of

the spray dry format, which is excellent in terms not only of the precursor powder handling friendliness but also of mass producibility, is optimal for the synthesis of an active material.

[0015]

(Problems to be solved by the invention)

Co, Ni, etc. used for these active materials, however, are rather expensive metal elements, and in particular, not only is Co expensive but it is also a strategically designated substance due to limited resources, and its supply sources must therefore be taken into full consideration, which represents a major issue to be addressed in the future. In other words, a group of substances characterized by the composition of βFe_2O_4 (wherein β is a cation), or so-called "ferrites," are being used extensively for magnets, magnetic devices, magnetic recording heads, magnetic recording media, etc., whereas, despite the uses, together with Fe, of expensive metal elements such as Co, /4 Ni, etc. as constituent components, consumed products are casually discarded, and no attempts are being made to effectively recycle such discarded matters at present.

[0016]

One objective of the present invention, which has been conceived for solving the foregoing problems, is to provide an anodic active material characterized by a homogeneous composition as well as a method for manufacturing an anodic active material wherein the targeted product can be easily obtained in a mass

producible fashion by using a ferrite. Another objective, furthermore, is to provide a lithium ion secondary battery endowed with excellent performances by using the aforementioned anodic active material.

[0017]

(Mechanism for solving the problems)

The first method of the present invention for manufacturing an anodic active material is a method inclusive of a process whereby a solution into which a composite oxide that includes, as a main component, a composition represented by the following general formula: AFe_2O_4 (in the formula, A signifies Mn, Fe, Zn, Co, Ni, or Cr) has been solubilized and another solution wherein an inorganic salt that includes a lithium ion, an inorganic salt that includes at least one type of first metal element ion(s) selected from among Co, Ni, Mn, and Fe, and a complexifying agent that forms a complex of lithium and the aforementioned first metal element(s) are mixed with one another in such a way that the ratio of lithium ions and ions of the aforementioned first metal element(s) will be 1 : x ($0.5 \leq x \leq 1.0$) are obtained, a process whereby a precursor is obtained by removing the solvent(s) of the aforementioned solutions by means of a spray dry, and a process whereby the aforementioned precursor is thermally treated.

[0018]

The second method of the present invention for manufacturing an anodic active material is a method wherein, with regard to the

aforementioned first method for manufacturing an anodic active material, the inorganic salt that includes a lithium ion is lithium nitrate, lithium sulfate, lithium chloride, lithium fluoride, lithium acetate, or lithium hydroxide.

[0019]

The third method of the present invention for manufacturing an anodic active material is a method wherein, with regard to the aforementioned first or second method for manufacturing an anodic active material, the inorganic salt that includes the first metal element ion(s) is a nitrate, sulfate, chloride, acetate, fluoride, or hydroxide.

[0020]

The fourth method of the present invention for manufacturing an anodic active material is a method wherein, with regard to any one of the aforementioned first through third methods for manufacturing an anodic active material, the complexifying agent is oxalic acid, tartaric acid, citric acid, succinic acid, malonic acid, or maleic acid.

[0021]

The first anodic active material of the present invention is obtained by any one of the aforementioned first through fourth manufacturing methods and includes a main component represented by the following general formula: LiM_xO_2 (in the formula, M is Co, Ni, Mn, or Fe, whereas $0.5 \leq x \leq 1.0$).

[0022]

The second anodic active material of the present invention is obtained by any one of the aforementioned first through fourth manufacturing methods by using a composite oxide which includes $CoFe_2O_4$ and $NiFe_2O_4$ as main components.

[0023]

The third anodic active material of the present invention is obtained by any one of the aforementioned first through fourth manufacturing methods by using a composite oxide which includes $MnFe_2O_4$ as a main component.

[0024]

The first lithium ion secondary battery of the present invention is characterized as follows: In a lithium ion secondary battery constituted to possess an anodic active material layer, a cathodic active material layer, and a separator which retains a non-aqueous electrolyte inclusive of a lithium ion and which is configured between the aforementioned anodic and cathodic active material layers, the aforementioned anodic active material layer includes the anodic active material specified in any one of Claims 5 through 7.

[0025]

(Application embodiments of the invention)

Application Embodiment 1

The method of Application Embodiment 1 of the present invention for manufacturing an anodic active material is a method

inclusive of a process whereby a solution into which has been dissolved a composite oxide that includes a composition represented by the following general formula: AFe_2O_4 (in the formula A is Mn, Fe, Zn, Co, Ni, or Cr) as a main component (referred alternatively to "ferrite") and another solution wherein an inorganic salt that includes a lithium ion, an inorganic salt that includes at least one type of first metal element ion(s) selected from among Co, Ni, Mn, and Fe (transition metal elements), and a complexifying agent that forms a complex of lithium and the aforementioned first metal element(s) are mixed with one another in such a way that the ratio of lithium ions and ions of the aforementioned first metal element(s) will be 1 : x ($0.5 \leq x \leq 1.0$) are obtained, a process whereby a precursor is obtained by removing the solvent of the aforementioned solutions by means of a spray dry, and a process whereby the aforementioned precursor is thermally treated. In this case, an anodic active material endowed with favorable performances can be manufactured in that A of the composite oxide expressed by the composition AFe_2O_4 is Mn, Fe, Zn, Co, Ni, or Cr.

[0026]

Lithium nitrate, lithium sulfate, lithium chloride, lithium fluoride, lithium acetate, or lithium hydroxide can, furthermore, be used as the inorganic salt which includes a lithium ion.

[0027]

Nitrates, sulfates, chlorides, acetates, fluorides, or hydroxides can, furthermore, be used as inorganic salts which

include the first metal element (transition metal element) ions. In this case, the "first metal element" mainly encompasses constituent components of the active material such as Co, Ni, Mn, Fe, etc., although cases where other metals are added for the purpose of improving performances are also conceivable. Extremely large numbers of the aforementioned optionally added metal elements such as miniscule quantitative ratios of Al, Ti, Mg,, Zn, V, Ba, Mg, Sr, Ca, etc. have already been proposed.

[0028]

Ones which are soluble with water and which possess hydroxyl or carboxyl groups capable of forming complexes with the lithium ion and transition metal ion with ease, furthermore, are desirable as the complexifying agent, and as such, organic acids (e.g., oxalic acid, tartaric acid, citric acid, succinic acid, malonic acid, maleic acid, etc.) can be used. EDTA (ethylenediaminetetraacetic acid), HEDTA (hydroxyethylenediaminetriacetic acid), etc. may also seem plausible as complexifying agents capable of forming complexes, but in cases where they are used, residual nitrogen-containing compounds persist in the precursor interior, and since they contribute to the disorder of crystals, battery performances deteriorate, which is problematic.

[0029]

It has already been publicly well-known in the field of ceramic powder synthesis, etc. that the spray dry method used in the present invention is an excellent method in terms of mass

producibility in comparison with the above-mentioned wet method, and it becomes possible, by using this method, to synthesize a large quantity of an active material precursor in an efficient fashion. After the spray dry operation, furthermore, the precursor can be recovered as an organic acid composite complex salt of the lithium and transition metal in a water- and/or solvent-free state, and therefore, the dried precursor can be handled with extreme ease. The spray temperature during the spray dry operation, furthermore, is designated within a range of 160 ~ 220°C, preferably 180 ~ 200°C. In a case where the temperature is lower than this range, it becomes impossible to sufficiently dry the precursor, and the persistence of residual crystalline water and humidity absorption become conspicuous. In a case where the temperature exceeds said range, furthermore, the reaction unabatedly progresses to the extent that the product composite complex becomes pyrolyzed, as a result of which it becomes converted, once again, into a highly hygroscopic oxide, and not only does it become impossible to achieve the essential objective of mixing homogeneity, but the precursor yield also decreases, accompanied by a significantly aggravated handling friendliness. A favorable active material, furthermore, becomes eventually obtained in a case where the spray pressure during the spray dry operation is designated within a range of 0.5 ~ 2.0 Pa.

[0030]

In a case where a discarded ferrite refuse was used as a source for the respective constituent elements of the active material such as Co, Ni, Mn, Fe, etc. according to the method of the first application embodiment of the present invention for manufacturing an anodic active material and where an active material was manufactured from a solution obtained by solubilizing the same, an anodic active material endowed with favorable performances was obtained. It was discovered anew, furthermore, that Fe, which is a constituent element of ferrite, does not hinder the performances of the active material.

[0031]

In other words, as far as the present application embodiment is concerned, it becomes possible, by partially feeding active material constituent components in the form of a solution obtained as a result of the solubilization of a previously consumed oxide product, namely ferrite, by forming a composite complex under the pervasion of a complexifying agent, and by instantaneously removing the solvent in a state where the homogeneous ionic mixing state is being perpetuated under the pervasion of said composite complex, to obtain an active material precursor without being adversely affected by the residual water content and/or solvent in the precursor interior or by the water content of air. It becomes possible, by baking this precursor, to obtain a high-performance active material and to achieve high battery performances.

[0032]

The aforementioned precursor, furthermore, is extremely homogeneous, and since no residual impurity components (e.g., water content, solvent, etc.) remain in its interior, its reactivity is excellent, based on which a baking temperature lower than the baking temperature of an ordinary dry method by approximately 50°C ~ 150°C becomes feasible. Since the baking temperature can thus be lowered, furthermore, it becomes possible to prevent the scatter of the lithium component, namely the active material, during the baking operation and to obtain an ideal active material true to the stoichiometric composition, which in turn contributes to improved battery performances. The optimal baking temperature of the active material, however, differs depending on the types of active materials, and although a range of 600 ~ 850°C can be generally postulated, the present invention is not limited to this temperature range.

[0033]

The size of the obtained active material can be arbitrarily controlled by adjusting the boiling point of the spray solution, spray temperature, spray pressure, double-fluid nozzle diameter, etc. In this case, however, there is no need to limit the shape and particle size of the active material synthesized in the present invention, and active materials of all specifications can be used.

[0034]

Application Embodiment 2

The anodic active material of the second application embodiment of the present invention includes a main component expressed by the following general formula: LiM_xO_2 (in the formula, M is Co, Ni, Mn, or Fe, whereas $0.5 \leq x \leq 1.0$), and it can be obtained by the manufacturing method of Application Embodiment 1.

[0035]

It is also possible, furthermore, to obtain an anodic active material which includes $Li(Co,Ni)O_2$ as a main component by using a composite oxide which includes $CoFe_2O_4$ and $NiFe_2O_4$ as main components according to procedures otherwise identical to those in Application Embodiment 1.

[0036]

It is also possible, furthermore, to obtain an anodic active material which includes $MnFe_2O_4$ as a main component by using a composite oxide which includes $LiMn_2O_4$ as a main component according to procedures otherwise identical to those in Application Embodiment 1.

[0037]

In a case where the molar ratio of the first metal element that forms a composite oxide with lithium is designated within a range of 0.5 ~ 1.0 with respect to lithium in the aforementioned application embodiments, furthermore, an excellent anodic capacitance can be achieved, whereas the capacitance decreases in a case where said ratio is lower than 0.5 or higher than 1.0.

[0038]

Application Embodiment 3

Figure 1 is a constitutional diagram pertaining to a general lithium ion secondary battery, and the notations denote the following in this figure: (1): Anodic active material layer; (2): Anodic collector; (3): Anodic case; (4): Gasket made of an insulating material; (5): Separator in which a non-aqueous electrolyte inclusive of lithium ions is being retained; (6): Cathodic active material layer; (7): Cathodic collector; (8): Cathodic case, whereas said separator (5), in which a non-aqueous electrolyte inclusive of lithium ions is being retained, is configured between the anodic active material layer (1) and the cathodic active material layer (6), and as far as the present application embodiment is concerned, the aforementioned anodic active material layer (1) possesses the anodic active material of the aforementioned Application Embodiment 2.

[0039]

(Application examples)

In the following, application examples will be explained in detail.

Application Example 1

$CoFe_2O_4$ was selected as a ferrite, and a solution was prepared by solubilizing it into hydrochloric acid at a concentration of 0.1 M/L. Next, an aqueous solution wherein the respective concentrations of lithium nitrate & cobalt nitrate

powders and of tartaric acid had been adjusted at 0.2 M/L each was prepared. These components were measured at their requisite volumetric ratios in compliance with the stoichiometric ratio of the $LiCoO_2$ active material and mixed in a solution state. After the contents had been agitated for 30 min. in this state, the obtained mixture was spray-dried by using a spray dryer. The liquid spray operation was carried out by using a double-fluid nozzle under the co-pervasion of compressed air, whereas the liquid pumping rate and spray pressure were respectively designated at 100 mL/min. and 2.0 MPa. The spray temperature was designated at 200°C, and an active material precursor was obtained in a yield of 95% or higher.

[0040]

After the precursor powder had been dried, it was packed into a quartz boat and then baked in the open atmosphere at 800°C over a 10-hour period, as a result of which a blackish brown powder was obtained. It was verified as a result of X ray diffraction analysis that the active material obtained in this application example of the present invention was an $LiCoO_2$ to which Fe had been added.

[0041]

Next, a lithium ion secondary battery the structure of which is shown in Figure 1 was prepared by using the active material obtained according to the aforementioned procedures. 90 wt% of this active material, 5 wt% of an acetylene black with an average particle size of 3.0 μm, which served as an electroconductive

material, and 5 wt% of polyvinylidene fluoride (PVDF), which served as a binding material (binder) component, were measured within a globe box surrounded /6 by an argon atmosphere, and a paste was prepared by mixing them with N-methylpyrrolidone (NMP), which served as a solvent. After this paste had been coated on an aluminum foil which had been prepared as the anodic collector (2) based on the doctor blade method, it was dried in a vacuum within a 150°C oven, and after it had been pressed, the anodic active material layer (1) was obtained.

[0042]

Metallic lithium was prepared as the cathodic active material layer (6), and it was filled into the cathodic case (8) together with the cathodic collector (7). A solution of an ethylene carbonate (EC)/1,2-dimethoxyethane (DME)/1.0 M lithium perchlorate mixture was prepared as an electrolytic solution, and after it had been impregnated into the separator (5) made of polypropylene (PP), [the impregnated separator was] sandwiched between the cathodic active material layer (6) and the anodic active material layer (1), and after the obtained structure had been inserted into the anodic case (3) together with the anodic collector (2), said case was sealed with the gasket (4), as a result of which a coin-shaped battery the structure of which is shown, as mentioned earlier, in Figure 1 was obtained. The obtained coin-shaped battery was termed as the "sample A."

[0043]

This battery was subjected to recharge & discharge measurements in the constant current mode at a current density of 0.1 mA/cm^2, as a result of which the results shown in Table I were obtained. In the above, the upper limit of the recharge voltage was set at 4.2 V.

[0044]

Table I

	Application Examples		Comparative Examples			
	Discharge capacitance (mAh/g)		Discharge capacitance (mAh/g)			
1	A	167	R1	138	RF1	140
2	B	195	R2	155	RF2	152
3	C	190	R3	168	RF3	167
4	D	140	R4	124	RF4	125
5	E	191	R5	159	RF5	156
6	F	137	R6	119	RF6	111

[0045]

Application Example 2

$NiFe_2O_4$ was selected as a ferrite, and a solution was prepared by solubilizing it into hydrochloric acid at a concentration of 0.1 M/L. Next, an aqueous citric acid solution wherein the respective concentrations of lithium acetate, nickel acetate, and citric acid had been adjusted at 0.2 M each was prepared. These solutions were measured at the requisite volumetric ratios in compliance with the stoichiometric ratio of the $LiNiO_2$ active material and then mixed in a solution state. The obtained mixture was agitated for 30 min. in this state and then spray-dried by using a spray dryer according to procedures identical to those in Application Example 1. The liquid spray operation was carried out by using a double-fluid nozzle under the co-pervasion of compressed air, whereas the liquid pumping rate and spray pressure were respectively designated at 100 mL/min. and 1.5 MPa. The spray temperature was designated at 190°C, and an active material precursor was obtained in a yield of 95% or higher.

[0046]

After the precursor powder had been dried, it was packed into a quartz boat and then baked in an oxygen atmosphere at 700°C over a 10-hour period, as a result of which a blackish brown powder was obtained. It was verified as a result of X ray diffraction analysis that the active material obtained in this application example of the present invention was an $LiNiO_2$ to which Fe had been added.

[0047]

A coin-shaped battery was prepared by using this active material according to procedures otherwise identical to those in Application Example 1 (this coin-shaped battery was termed as the "sample B"), and the results of recharge & discharge measurements conducted according to similar procedures are shown in Table I.

[0048]

Application Example 3

Powders of $NiFe_2O_4$ and $CoFe_2O_4$ were provided as ferrites, and a solution was prepared by solubilizing them into an acid mixture of hydrochloric acid and nitric acid at a concentration of 0.1 M/L. Next, an aqueous solution wherein the respective concentrations of lithium chloride, cobalt chloride, nickel chloride, and oxalic acid had been adjusted at 0.2 M each was prepared. These solutions were measured at the requisite volumetric ratios in compliance with the stoichiometric ratio of an $LiCo_{0.2}Ni_{0.8}O_2$ active material and then mixed in a solution state. The obtained mixture was agitated for 30 min. in this state and then spray-dried according to procedures identical to those in Application Example 1. The spray temperature was designated at 220°C, and an active material precursor was obtained in a yield of 95% or higher.

[0049]

After the precursor powder had been dried, it was packed into a quartz boat and then baked in the atmosphere at 750°C over a 10-

hour period, as a result of which a blackish brown powder was obtained. It was verified as a result of X ray diffraction analysis that the active material obtained in this application example of the present invention was an $LiCo_{0.2}Ni_{0.8}O_2$ to which Fe had been added.

[0050]

A coin-shaped battery was prepared by using this active material according to procedures otherwise identical to those in Application Example 1 (this coin-shaped battery was termed as the "sample C"), and the results of recharge & discharge measurements conducted according to similar procedures are shown in Table I.

[0051]

Application Example 4

An $MnFe_2O_4$ magnet was prepared as a ferrite, and it was electrolyzed and solubilized, as an anode, within dilute hydrochloric acid under the co-pervasion of platinum as a cathode, as a result of which a solution with a concentration of 0.1 M/L was obtained. Next, an aqueous solution wherein the respective concentrations of lithium sulfate, manganese nitrate, and malonic acid had been adjusted at 0.2 M each was prepared. These solutions were measured at the requisite volumetric ratios in compliance with the stoichiometric ratio of an $LiMn_2O_4$ active material and then mixed in a solution state. The obtained mixture was agitated for 30 min. in this state and then spray-dried according to procedures identical to those in Application Example

1. The spray temperature was designated at 180°C, and an active material precursor was obtained in a yield of 95% or higher.

[0052]

After the precursor powder had been dried, it was packed into a quartz boat and then baked in the open atmosphere at 800°C over a 10-hour period, as a result of which a blackish brown powder was obtained. It was verified as a result of X ray diffraction analysis that the active material obtained in this application example of the present invention was an $LiMn_2O_4$ to which Fe had been added.

[0053]

A coin-shaped battery was prepared by using this active material according to procedures otherwise identical to those in Application Example 1 (this coin-shaped battery was termed as

/7

the "sample D"), and the results of recharge & discharge measurements conducted according to similar procedures are shown in Table I.

[0054]

Application Example 5

An $(Ni,Zn)Fe_2O_4$ bar was provided as a ferrite, and it was solubilized into an acid mixture identical to that used in Application Example 3 at a concentration of 0.1 M/L, as a result of which a solution was prepared. Next, an aqueous solution wherein the concentration of lithium hydroxide had been adjusted

at 0.2 M was prepared. Next, 0.2 M equivalent of nickel hydroxide was solubilized into an aqueous solution wherein the concentration of citric acid had been adjusted at 0.2 M, as a result of which an aqueous citric acid solution inclusive of nickel ions was prepared. Both solutions were measured at their respective requisite volumetric ratios in compliance with the stoichiometric ratio of an $LiNiO_2$ active material and then mixed in a solution state. The obtained mixture was agitated for 30 min. in this state and then spray-dried according to procedures identical to those in Application Example 1. The spray temperature was designated at 210°C, and an active material precursor was obtained in a yield of 95% or higher.

[0055]

After the precursor powder had been dried, it was packed into a quartz boat and then baked in an oxygen atmosphere at 700°C over a 10-hour period, as a result of which a blackish brown powder was obtained. It was verified as a result of X ray diffraction analysis that the active material obtained in this application example of the present invention was an $LiNiO_2$ to which Fe and Zn had been added.

[0056]

A coin-shaped battery was prepared by using this active material according to procedures otherwise identical to those in Application Example 1 (this coin-shaped battery was termed as the "sample E"), and the results of recharge & discharge measurements conducted according to similar procedures are shown in Table I.

[0057]

Application Example 6

An $(Mn,Zn)Fe_2O_4$ powder was selected as a ferrite, and it was solubilized into hydrochloric acid at a concentration of 0.1 M/L, as a result of which a solution was prepared. Next, an aqueous succinic acid solution wherein the respective concentrations of lithium nitrate, manganese nitrate, and succinic acid had been adjusted at 0.2 M each was prepared. The respective solutions were measured at the requisite volumetric ratios in compliance with the stoichiometric ratio of an $LiMn_2O_4$ active material and then mixed in a solution state. The obtained mixture was agitated for 30 min. in this state and then spray-dried according to procedures identical to those in Application Example 1. The spray temperature was designated at 220°C, and an active material precursor was obtained in a yield of 95% or higher.

[0058]

After the precursor powder had been dried, it was packed into a quartz boat and then baked in the open atmosphere at 800°C over a 10-hour period, as a result of which a blackish brown powder was obtained. It was verified as a result of X ray diffraction analysis that the active material obtained in this application example of the present invention was an $LiMn_2O_4$ to which Fe and Zn had been added.

[0059]

A coin-shaped battery was prepared by using this active material according to procedures otherwise identical to those in Application Example 1 (this coin-shaped battery was termed as the "sample F"), and the results of recharge & discharge measurements conducted according to similar procedures are shown in Table I.

[0060]

Comparative Example 1

The respective requisite quantitative ratios of lithium carbonate and cobalt oxide in compliance with the stoichiometric ratio of the active material of Application Example 1 were measured and then mixed within a ball mill over a 2-hour period based on the dry method, which is the most general manufacturing method in the prior art. After it had been packed into a quartz boat, it was baked in the open atmosphere at 900°C over a 10-hour period, as a result of which a blackish brown active material (it was termed as the "sample r1") was obtained. In a separate lot, furthermore, the respective powders of lithium carbonate and cobalt oxide were charged, based on a wet method of the prior art, into and mixed within the ferrite solution prepared in Application Example 1 in compliance with the stoichiometric ratio of the active material of Application Example 1, and the obtained solution was dried, packed into a quartz boat, and then baked in the open atmosphere at 900°C over a 10-hour period, as a result of

which a blackish brown powder (it was termed as the "sample rf1") was obtained.

[0061]

Coin-shaped batteries were prepared by using these two types of active materials (r1 & rf1) according to procedures otherwise similar to those in Application Example 1 (these coin-shaped batteries were respectively termed as samples "R1" & "RF1"), and the results of recharge & discharge measurements conducted according to similar procedures are shown in Table I.

[0062]

Comparative Example 2

As in Comparative Example 1, the respective requisite quantitative ratios of lithium carbonate and nickel hydroxide in compliance with the stoichiometric ratio of the active material of Application Example 2 were measured and then mixed with one another within a ball mill over a 2-hour period. Next, the obtained mixture was packed into a quartz boat and then baked in an oxygen atmosphere at 800°C over a 10-hour period, as a result of which a blackish brown powder (it was termed as the "sample r2") was obtained. In a separate lot, furthermore, the respective powders of lithium carbonate and nickel hydroxide were charged, based on the wet method of the prior art, into and mixed within the ferrite solution prepared in Application Example 2 in compliance with the stoichiometric ratio of the active material of Application Example 2, and the obtained solution was dried, packed

into a quartz boat, and then baked in the open atmosphere at 800°C over a 10-hour period, as a result of which a blackish brown powder (it was termed as the "sample rf2") was obtained.

[0063]

Coin-shaped batteries were prepared by using these two types of active materials (r2 & rf2) according to procedures otherwise similar to those in Application Example 1 (these coin-shaped batteries were respectively termed as samples "R2" & "RF2"), and the results of recharge & discharge measurements conducted according to similar procedures are shown in Table I.

[0064]

Comparative Example 3

The respective requisite quantitative ratios of lithium carbonate, nickel hydroxide, and cobalt hydroxide in compliance with the stoichiometric ratio of the active material of Application Example 3 were measured and then mixed with one another within a ball mill over a 2-hour period based on the dry method, which represents the most general manufacturing method of the prior art. Next, the obtained mixture was packed into a quartz boat and then baked in the open atmosphere at 850°C over a 10-hour period, as a result of which a blackish brown powder (it was termed as the "sample r3") was obtained. In a separate lot, furthermore, the respective powders of lithium carbonate, nickel hydroxide, and cobalt hydroxide were charged, based on the wet method of the prior art, into and mixed within the ferrite

solution prepared in Application Example 3 in compliance with the stoichiometric ratio of the active material of Application Example 3, and the obtained solution was dried, packed into a quartz boat, and then baked in the open atmosphere at 850°C over a 10-hour period, as a result of which a blackish brown powder (it was termed as the "sample rf3") was obtained.

[0065]

Coin-shaped batteries were prepared by using these two types of active materials (r3 & rf3) according to procedures otherwise similar to those in Application Example 1 (these coin-shaped batteries were respectively termed as samples "R3" & "RF3"), and the results of recharge & discharge measurements conducted according to similar procedures are shown in Table I.

[0066]

<u>Comparative Example 4</u>

Certain quantitative ratios of lithium nitrate and manganese nitrate were measured and then added to and solubilized into ion-exchanged water, which had been metered in such a way that the concentrations of the respective ions would be 0.2 M each, as a result of which a mixed solution wherein the lithium and manganese ions thereof met the stoichiometric ratio of the active material of Application Example 4 was obtained. This solution was heated while being intensely agitated by using a magnetic stirrer, and after it had been enriched by evaporating the solvent, a precursor

was obtained. It was retrieved, dried in a vacuum at 200°C over a 2-hour period, packed into a /8 quartz boat, and then baked in the open atmosphere at 850°C over a 10-hour period, as a result of which a blackish brown powder (it was termed as the "sample r4") was obtained. In a separate lot, furthermore, the respective powders of lithium nitrate and manganese nitrate were charged, based on the wet method of the prior art, into and mixed within the ferrite solution prepared in Application Example 4 in compliance with the stoichiometric ratio of the active material of Application Example 4, and the obtained solution was dried, packed into a quartz boat, and then baked in the open atmosphere at 850°C over a 10-hour period, as a result of which a blackish brown powder (it was termed as the "sample rf4") was obtained.

[0067]

Coin-shaped batteries were prepared by using these two types of active materials (r4 & rf4) according to procedures otherwise similar to those in Application Example 1 (these coin-shaped batteries were respectively termed as samples "R4" & "RF4"), and the results of recharge & discharge measurements conducted according to similar procedures are shown in Table I.

[0068]

Comparative Example 5

Certain quantitative ratios of lithium nitrate and nickel nitrate were measured and then added to and solubilized into ion-

exchanged water, which had been metered in such a way that the concentrations of the respective ions would be 0.2 M each, as a result of which a mixed solution wherein the lithium and nickel ions thereof met the stoichiometric ratio of the active material of Application Example 5 was obtained. An aqueous citric acid solution the concentration of which had been adjusted at 0.2 M was further added to this solution. After the solvent had been evaporated, by using a rotary evaporator, from the obtained mixture within a 60°C hot water bath at a reduced pressure of 1,000 Pa, the obtained residue was gelled over a 48-hour period. It was retrieved, dried in a vacuum at 200°C over a 2-hour period, packed into a quartz boat, and then baked in the open atmosphere at 750°C over a 10-hour period, as a result of which a blackish brown powder (it was termed as the "sample r5") was obtained. In a separate lot, furthermore, the respective powders of lithium nitrate and nickel nitrate were charged, based on the wet method of the prior art, into and mixed within the ferrite solution prepared in Application Example 5 in compliance with the stoichiometric ratio of the active material of Application Example 5, and the obtained solution was dried, packed into a quartz boat, and then baked in the open atmosphere at 750°C over a 10-hour period, as a result of which a blackish brown powder (it was termed as the "sample rf5") was obtained.

[0069]

Coin-shaped batteries were prepared by using these two types of active materials (r5 & rf5) according to procedures otherwise similar to those in Application Example 1 (these coin-shaped batteries were respectively termed as samples "R5" & "RF5"), and the results of recharge & discharge measurements conducted according to similar procedures are shown in Table I.

[0070]

Comparative Example 6

Certain quantitative ratios of lithium acetate and manganese acetate were measured and then added to and solubilized into ion-exchanged water, which had been metered in such a way that the concentrations of the respective ions would be 0.2 M each, as a result of which a mixed solution wherein the lithium and manganese ions thereof met the stoichiometric ratio of the active material of Application Example 6 was obtained. An aqueous ethylene glycol solution the concentration of which had been adjusted at 0.4 M was further added to this solution. The obtained mixture was heated within a 90°C hot water bath while being intensely agitated for inducing the evaporation of the solvent, and a polymerizing reaction was induced to progress over a 24-hour period. The obtained product was retrieved, dried in a vacuum at 150°C over a 2-hour period, packed into a quartz boat, and then baked in the open atmosphere at 850°C over a 10-hour period, as a result of which a blackish brown powder (it was termed as the "sample r6") was obtained. In a separate lot, furthermore, the respective

powders of lithium acetate and manganese acetate were charged, based on the wet method of the prior art, into and mixed within the ferrite solution prepared in Application Example 6 in compliance with the stoichiometric ratio of the active material of Application Example 6, and the obtained solution was dried, packed into a quartz boat, and then baked in the open atmosphere at 850°C over a 10-hour period, as a result of which a blackish brown powder (it was termed as the "sample rf6") was obtained.

[0071]

Coin-shaped batteries were prepared by using these two types of active materials (r6 & rf6) according to procedures otherwise similar to those in Application Example 1 (these coin-shaped batteries were respectively termed as samples "R6" & "RF6"), and the results of recharge & discharge measurements conducted according to similar procedures are shown in Table I.

[0072]

It can be inferred from Table I that the respective anodic active materials of Application Examples 1 ~ 6 are each endowed with discharge capacitances higher than that achieved in any comparative example. It is shown, furthermore, that no adverse effects are exerted on the discharge capacitance even in a case where either Fe or Fe and Zn are included in the aforementioned active material.

[0073]

Combinations of composite oxides characterized by the composition of AFe_2O_4 wherein A is Mn, Fe, Zn, Co, Ni, or Cr other than those prescribed in Application Examples 1 ~ 6, furthermore, were selected, and their discharge capacitances were comparatively investigated according to procedures similar to those of Application Examples 1 ~ 6 and Comparative Examples 1 ~ 6 of the present invention. As a result, it was demonstrated that, as in the aforementioned embodiments, the discharge capacitances of the anodic active materials of the present invention are higher by approximately 10 ~ 30 mAh/g.

[0074]

(Effects of the invention)

The first method of the present invention for manufacturing an anodic active material is a method inclusive of a process whereby a solution into which a composite oxide that includes, as a main component, a composition represented by the following general formula: AFe_2O_4 (in the formula, A signifies Mn, Fe, Zn, Co, Ni, or Cr) has been solubilized and another solution wherein an inorganic salt that includes a lithium ion, an inorganic salt that includes at least one type of first metal element ion(s) selected from among Co, Ni, Mn, and Fe, and a complexifying agent which forms a complex of lithium and the aforementioned first metal element(s) are mixed with one another in such a way that the ratio of lithium ions and ions of the aforementioned first metal element(s) will be 1 : x ($0.5 \leq x \leq 1.0$) are obtained, a process

whereby a precursor is obtained by removing the solvent of the aforementioned solutions by means of a spray dry, and a process whereby the aforementioned precursor is thermally treated, based on which an effect of easily achieving mass producibility by using a ferrite can be achieved.

[0075]

The second method of the present invention for manufacturing an anodic active material is a method wherein, with regard to the aforementioned first method for manufacturing an anodic active material, the inorganic salt that includes a lithium ion is lithium nitrate, lithium sulfate, lithium chloride, lithium fluoride, lithium acetate, or lithium hydroxide, based on which an effect of easily achieving mass producibility by using a ferrite can be achieved. /9

[0076]

The third method of the present invention for manufacturing an anodic active material is a method wherein, with regard to the aforementioned first or second method for manufacturing an anodic active material, the inorganic salt that includes the first metal element ion(s) is a nitrate, sulfate, chloride, acetate, fluoride, or hydroxide, based on which an effect of easily achieving mass producibility by using a ferrite can be achieved.

[0077]

The fourth method of the present invention for manufacturing an anodic active material is a method wherein, with regard to any one of the aforementioned first through third methods for

manufacturing an anodic active material, the complexifying agent is oxalic acid, tartaric acid, citric acid, succinic acid, malonic acid, or maleic acid, based on which an effect of easily achieving mass producibility by using a ferrite can be achieved.

[0078]

The first anodic active material of the present invention is obtained by any one of the aforementioned first through fourth manufacturing methods and includes a main component represented by the following general formula: LiM_xO_2 (in the formula, M is Co, Ni, Mn, or Fe, whereas $0.5 \leq x \leq 1.0$), based on which an effect of homogenizing the composition can be achieved.

[0079]

The second anodic active material of the present invention is obtained by any one of the aforementioned first through fourth manufacturing methods by using a composite oxide which includes $CoFe_2O_4$ and $NiFe_2O_4$ as main components, based on which an effect of homogenizing the composition can be achieved.

[0080]

The third anodic active material of the present invention is obtained by any one of the aforementioned first through fourth manufacturing methods by using a composite oxide which includes $MnFe_2O_4$ as a main component, based on which an effect of homogenizing the composition can be achieved.

[0081]

The first lithium ion secondary battery of the present invention is characterized as follows: In a lithium ion secondary

battery constituted to possess an anodic active material layer, a cathodic active material layer, and a separator which retains a non-aqueous electrolyte inclusive of a lithium ion and which is configured between the aforementioned anodic and cathodic active material layers, the aforementioned anodic active material layer includes any of the aforementioned first through third anodic active materials, based on which an effect of ensuring excellent performances can be achieved.

Brief explanation of the figures

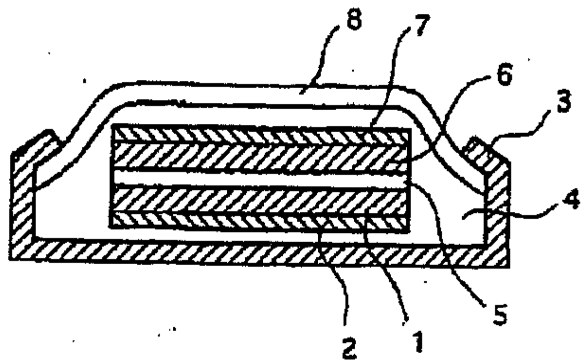
Figure 1: A circuit diagram pertaining to a general coin-shaped battery.

(Explanation of notations)

(1): Anodic active material layer; (2): Anodic collector; (5): Separator; (6): Cathodic active material layer; (7): Cathodic collector.

Figure 1

【図1】



[(1): Anodic active material layer; (2): Anodic collector; (5): Separator; (6): Cathodic active material layer; (7): Cathodic collector]